Development of Concurrent grinding for application in aqueous mineral carbonation

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ABSTRACT

Vast reserves of peridotite and serpentinite rocks can be utilised for the safe and permanent sequestration of global CO_2 emissions via aqueous mineral carbonation. These, and indeed most feedstocks used in mineral carbonation require ultrafine grinding and/or heat-activation, to engender significantly enhanced reactivity in the rock such that it can then be carbonated. Both activation processes are energy intensive and present significant obstacles to the commercial application of mineral carbonation. Here we show that these limitations can be addressed, at least in part, through the application of a concurrent or *in operando* grinding technique which does not require feedstocks which have been subjected to prior ultrafine grinding nor heat-activation.

Concurrent grinding is shown to result in a significant increase in magnesite yields for non-heat activated feedstock, prepared such that fines (<20 μm particles) were excluded from the feed. We assert that concurrent grinding may be a suitable technique for the processing of feedstocks such as those containing significant proportions of forsterite and pyroxene, minerals which are unresponsive to thermal activation for use in aqueous mineral carbonation. This study also investigates the effect of different grinding media particle size on reducing the particle size distribution (PSD) of the feed. Optimum ratio of grinding media size to feed particle size, optimum grinding media and slurry concentrations, optimum time for grinding and optimum impeller designs are determined for the system under study. The quantitative effect of grinding media concentration, slurry concentration, pressure and temperature on magnesite yield has been investigated.

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1. Introduction

It has been predicted (Shaffer, 2010) that under a "business-as-usual" emission scenario, average atmospheric temperatures will rise by 5 °C by 2130 CE and ocean warming will be more than 3 °C by 4010 CE. These predictions underscore the importance of mitigating anthropogenic CO_2 emissions.

Lackner (2003) has pointed out that carbon can be stored as mineral carbonates for more than 100 000 years. One important challenge to implement mineral carbonation technology is relatively low magnesite yields which are generally observed, which has been attributed to limitations in the extent of extraction of magnesium from large feed particles caused by the development of a silica-rich layer (10—20 Å thick) on particle surfaces during reaction (Béarat et al., 2006; Jarvis et al., 2009; King et al., 2010; Pokrovsky and Schott, 2000). Various approaches have been used to increase the rate and extent of mineral dissolution such as reducing the size of particles, increasing the extraction temperature, decreasing the pH of the extraction conditions, the use of a heat-treatment pre-extraction activation technique (Farhang et al., 2016, 2017; Hariharan and Mazzotti, 2017; Hariharan et al., 2014; Werner et al., 2014), the addition of additives or catalysts and the adoption of concurrent grinding.

Park and Fan (Park and Fan, 2004; Park et al., 2003) studied internal grinding using glass beads as grinding media, high intensity sound acoustics and sonication to exfoliate the silica-rich layers. They employed a fluidised bed reactor with grinding media, where their research was related to a pH-swing process rather than single stage aqueous mineral carbonation (Connor et al.,

2005). They found that glass media invoked the refreshing of the particle surfaces and resulted in an enhanced level of Mg extraction. Arizona State University (ASU) researchers utilised sonication and concurrent grinding using quartz to exfoliate the silica-rich layers during aqueous mineral carbonation of olivine and observed an increase in magnesite yield from 68% to 84% which was attributed to concurrent (*in operando*[1]) grinding (Chizmeshya et al., 2007; Béarat et al., 2006). Bodenan et al. (Bodénan et al., 2014) and Julcour et al. (2015) employed 1.3 mm alumina and 1 mm zirconia beads to exfoliate silica-rich layers during aqueous mineral carbonation of sub 100 μm feedstock and found a significant increase in magnesite yields was achieved when beads were used. Their feedstock consisted of a significant fraction of fine particles ($d_{50} = 20$ μm, $d_{32} = 4.1-4.7$ μm) and they employed a partial heat-treatment to the feedstock. As such there is some uncertainty with respect to the influence the grinding media (compared to the heat-activation step) had on the magnesite yield. They employed a high fraction of grinding media (300 g in 300 ml reactor), and used a relatively dilute slurry (9 wt% solids) with the concurrent grinding performed for 24 h. The long timescale (24 h), fine grinding of the feedstock ($d_{50} = 20$ μm), heat-treatment, the high media and low slurry concentrations would all pose serious challenges with respect to the feasibility and implementation for any commercial process adopting these experimental conditions.

Julcour et al. (Julcour et al., 2015) have acknowledged that concurrent grinding requires further development, and the current research is focussed on the development of a concurrent grinding technique with regards to the type of grinding media, media size, media and slurry concentrations, impeller designs for media stirring, impeller length, optimum operating temperature and pressure and grinding/reaction time. This study also focusses on using raw feedstocks for mineral carbonation in the absence of any heat-activation pre-treatment of the feedstock. A literature review has been conducted on stirred bead milling used for mineral processing applications, and adopting these techniques to the aqueous mineral carbonation process. To determine the optimum operating temperature, pressure, time, grinding media and slurry concentrations, a wide range of operating parameters has been examined by adopting a statistical experimental design strategy based on the Placket-Burman technique (Placket and Burman, 1946). In this experimental design approach, important variables with nominal (low) and extreme (high) values are chosen and their quantitative effect on magnesite yield is determined.

2. Material, methods and experimental set-up

2.1. Material

Dunite rock for this study was collected from The Great Serpentine Belt, NSW, Australia. The initial feed size of the rock was 2–3 mm which was then ground in a ball mill (roller ball mill, MTI Corporation, USA) followed by wet sieving to obtain a 20-45 μm fraction where fines (particles < 10 μm) were essentially absent. Seven different batches of feed material were prepared, having similar and definite size "bins"[2] (average $d_{10} = 27$ μm, $d_{50} = 42$ μm, $d_{90} = 64$ μm). This 20–45 μm size bin of dunite feed was analysed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) analysis (Mg = 27.3%, Si = 17.7%, Fe = 6.76%), and by X-Ray Diffraction (XRD) and the phases identified in the samples were lizardite, olivine, brucite and magnetite. The composition of this material, as determined by a combination of semi-quantitative XRD and Thermogravimertic-Mass Spectrometer (TGA-MS) analysis, is as follows; lizardite (51–53%), olivine (41–43%), brucite (5.3–5.9%) and magnetite (0.46–0.5%). A Setsys Evolution 1200 TGA-DSC was coupled with a Thermostar Quadrupole Mass Spectrometer in order to identify the evolved gases on heating. Dunite feed and carbonated products (6–7 mg) were heated from room temperature to 1000 °C with a temperature ramp of 5 °C/min (refer to Supplementary Information for magnesite yield calculation). XRD analyses were performed using a Philips X'Pert Pro multi-purpose diffractometer with Cu radiation and 2θ from 10 to 90°. Collection time used was 1 s with step size of 0.02°. Dunite feed, ground and carbonated samples are characterised by Scanning Electron Microscopy (SEM) (Zeiss Sigma VP FESEM). Particle size distribution (PSD) was measured using Malvern Mastersizer 2000 particle analyser.

2.2. Experimental set-up

A 300 mL reactor (Parr Instrument Company, USA; Model 4560) made of 316 stainless steel was used for single stage carbonation reactions (Fig. 1). The operating temperature range of the reactor was between 0 and 225 °C and operating pressure range was from 0 to 200 bar. The reactor was equipped with a controller for temperature and stirring control. A type-J thermocouple (Iron-Constantan) was used as a temperature sensor having an operating range of between 0 and 800 °C, with an accuracy of ±2 °C. The reactor has an inner coil loop for cooling of the slurry to provide temperature control and a magnetic stirrer (0–600 rpm) for stirring the slurry during reaction. A safety pressure relief valve (set at 206 bar) was installed on the reactor. The reactor was heated electrically by a 230 V, 510 W heating jacket. A pressure gauge was installed on the reactor to monitor the pressure inside the reactor and a CO_2 booster system (MAXIMATOR GmbH, Germany), driven by an air compressor, was connected to the reactor to pressurise it with CO_2. A large air piston was charged with the low pressure (5–6 psig) air which drives a small piston which compresses the CO_2 gas present inside the discharge cylinder. The booster operation was continued until the desired operating pressure (here 130 bar) was achieved.

Dunite slurry (typically 15 wt % solids in distilled water) was charged into the reactor, followed by reactor re-assembling. The reactor was then evacuated using a vacuum pump to remove any residual air present in the reactor. Control of the reaction initiation point is important to enable an evaluation of the reaction kinetics. Following reactor evacuation, heating of the reactor was commenced and, typically, continued up to the final reaction temperature of 180 °C. When the temperature stabilised, the reactor pressurised using the CO_2 booster control manifold, typically to 130 bar. An aliquot was taken from the reactor at this time, corresponding to time zero with respect to the overall reaction kinetic analysis. The sampler was used to withdraw small volume aliquots of the reacting slurry from the reactor over the duration of the experiment (Fig. 1). Prior to taking aliquots, valve B, valve D and valve A were closed, with valve C fully open. Valve A was opened slightly until the slurry was transferred into the sampler and then valve A was closed. Gas was released from the sampler by slowly opening valve B, and valve D was opened in order to collect the aliquot. Slurry was sampled from the reactor using the same procedure at different reaction time intervals. The sampler was flushed after each sample. Solids present in the sampler were removed by washing sampler with distilled water after each sample. Pressure

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[1] *in operando* is defined as under conditions in which grinding and carbonation take place simultaneously i.e. concurrently, while *In situ* means that grinding takes place initially in the absence of CO_2 and the carbonation reaction is performed in a subsequent step.

[2] A bin is a definite size range of particles e.g. 20–45 μm is a bin and is comprised of particles passing a 45 μm sieve and retained on a 20 μm sieve.
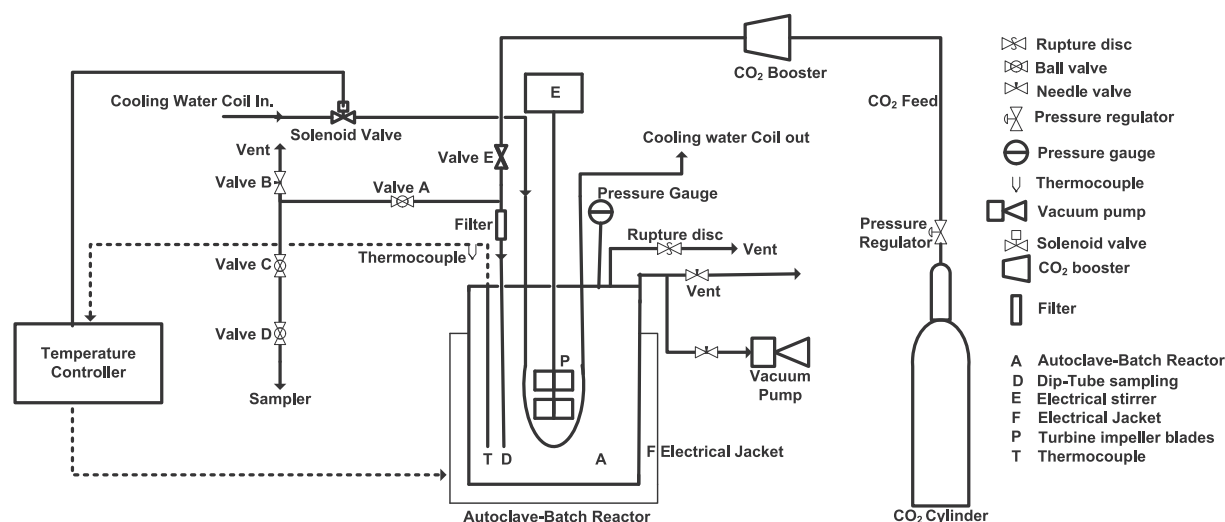
Fig. 1. Schematic of the mineral carbonation experimental facility.

was maintained at 130 bar otherwise it would decrease slightly (2–3 bar) during the reaction or slurry sampling from the reactor. Heating was switched off when the experiment was complete, and the reactor was cooled to 30 °C followed by depressurisation to atmospheric pressure. After depressurising, the reactor was opened to collect slurry. The supernatant solution was separated from the solids, and solids were washed and dried in an oven at 100 °C for 24 h.

2.3. Methods

2.3.1. Testing in acrylic reactor at ambient temperature and pressure

An acrylic reactor was used during initial screening of impellors, which was constructed from poly carbonate materials and has dimensions virtually identical to the Parr stainless steel reactor. Dunite slurry, of different compositions, was charged into the (transparent) reactor. The slurry was stirred and visual examination of the material during mixing was undertaken. Different impeller designs were explored to engender optimum stirring and agitation conditions by observing the vortex formation and the extent of solids mixing.

2.3.2. PSD testing in the absence of CO_2 pressure

Dunite slurry, of varying composition between experiments, was added to the stainless steel liner for the reactor (used to minimise excessive wear of the reactor vessel), along with grinding media and the reactor was then assembled. For experiments at room temperature, heating was not initiated and the stirrer was fixed at 600 rpm and the experiment proceeded for the predetermined time. At the end of each experiment, the reactor was opened, the slurry removed and the resulting PSD of the solid product was measured. For experiments performed at high

temperatures (180 °C), the slurry was added to the liner, along with grinding media and the reactor was then assembled. Stirring was initiated at 600 rpm and the reactor was heated to the desired temperature (180 °C) and the experiment was continued for the desired time (5 h, 2.5 h or 1 h).

2.3.3. Carbonation under CO_2 pressure

2.3.3.1. Reference experiments. In a reference experiments with dunite, the slurry was added to the reactor liner and the reactor was assembled and heated to 180 °C. The reactor was then pressurised with CO_2 to 130 bar and the carbonation reaction proceeded for the predetermined time.
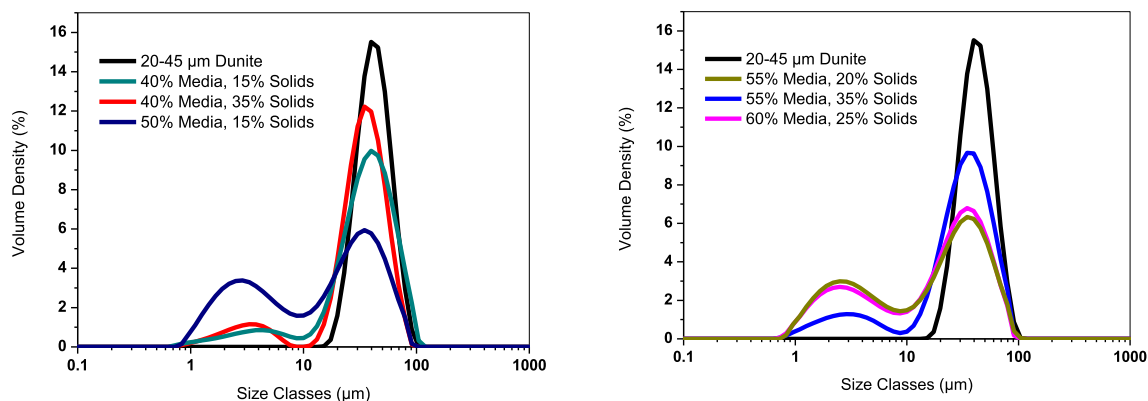
2.3.3.2. In situ grinding experiments. To conduct *in situ* (in the absence of CO_2) grinding experiments, the dunite slurry was charged into the reactor liner, along with grinding media. The reactor was assembled and heated to the desired temperature. *In situ* grinding was performed for a predetermined length of time. When an experiment was completed, the reactor was cooled to 50 °C and ground dunite slurry was removed and grinding media separated using a 200 μm sieve. In the second step, this ground slurry was added to the liner without grinding media and reactor was re-assembled. The reactor was heated to the desired temperature and pressurised with CO_2 to 65 or 130 bar and carbonation proceeded till the desired time was reached.

2.3.3.3. Concurrent (in operando) grinding experiments. In concurrent grinding experiments, the dunite slurry was charged into the reactor liner, along with grinding media. The reactor was assembled and heated to the desired temperature. The reactor was then pressurised with CO_2 to 65 or 130 bar and carbonation and grinding proceeded simultaneously for the desired time period.

Table 1
Overall slurry concentration and ratio of weight percentage of media to weight percentage of solids.

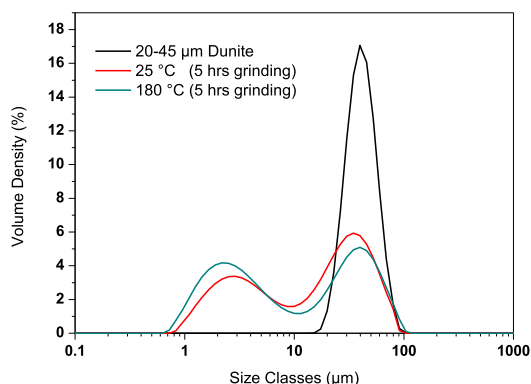| Sr.No.	Grinding media conc. (wt%)	Dunite solids conc. (wt%)	Overall slurry Conc. (wt%)	Mass Ratio (media/solids)
1	40	15	46	2.7
2	50	15	54	3.3
3	40	35	55	1.1
4	55	20	60	2.7
5	55	35	64	1.6
6	60	25	65	2.4

Fig. 2. PSD for 20–45 μm dunite feed and after 5 h concurrent grinding at ambient temperature and pressure using 0.5 mm zirconia as grinding media, 40 wt% and 50 wt% grinding media (left), 55 wt% and 60 wt% grinding media (right).

Table 2
PSD for 20–45 μm dunite feed and after 5 hrs concurrent grinding.

Time (h)	Mass of grinding media (wt%)	Solids conc. (wt%)	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)
0 (feed)	–	–	27	42	64
5	40	15	8.4	34	63
5	40	35	5.1	31	53
5	50	15	1.8	16	48
5	55	20	1.8	19	51
5	55	35	3.5	30	56
5	60	25	1.9	21	52

Fig. 3. PSD for 20–45 μm dunite feed and after 5 h concurrent grinding at room temperature (25 °C) and 180 °C using 0.5 mm zirconia as grinding media with 50 wt% media and 15 wt% solids concentration.

Table 3
PSD for 20–45 μm dunite feed and 5 h concurrent grinding at room temperature (25 °C) and 180 °C.

| Time (h)	Temperature (°C)	d_{10} μm	d_{50} μm	d_{90} μm
0 (feed)	–	27	42	64
5	25	1.8	16	48
5	180	1.4	8.7	51

3. Results and discussion

3.1. Examination of different impeller designs in clear acrylic reactor

The mixing behaviour of hollow and solid shaft turbine impellers, pitched turbine impellers with hollow and solid shaft and hollow rod type impellers with hollow shaft was studied in the acrylic (transparent) reactor. These experiments were undertaken in distilled water, slurries, various grinding media concentrations in distilled water and finally a combination of slurries and grinding media. Details of these experiments are provided in Supplementary Information document, Table S1 (distilled water only and slurries) and Supplementary Information Table S2 (grinding media in distilled water and combination of solid slurries and grinding media in distilled water). Experiments involving both grinding media and slurries were conducted at 600 rpm, as grinding media spheres were found to be ineffective at 300 rpm. For initial tests 0.5 mm zirconia beads were selected.

3.2. Study on establishing the optimum slurry concentration and ratio of media to dunite solids

Experiments using the clear acrylic reactor assisted in disclosing the appropriate combination of grinding media and solids concentrations (50 wt% media with 15 wt% solids, 40 wt% media with 15 wt% and 35 wt% solids, 55 wt% media with 20 wt% and 35 wt% solids, 60 wt% media with 25 wt% solids) as the initial experimental conditions for particle size reduction. Davis and Dawson (Davis and Dawson, 1989) suggested that the slurry concentration for grinding in stirred bead mills should be 50–60 wt% (including grinding media and solids) and that the percentage of grinding media should be at least double the percentage of solids, to generate a smaller particle size distribution. By examining selected combinations of grinding media and solids concentrations, a wide range of slurry concentration (46-65 wt%) and mass ratios (1.1–3.3) of grinding media to percent solids (Table 1) was studied. Particle size reduction for these selected combinations of grinding media to dunite solids (using 0.5 mm zirconia as grinding media) is presented in Fig. 2 and in Table 2. SEM micrographs of the 20–45 μm dunite feed and ground solids sampled from the reactor after 5 h, are presented in Supplementary Information Fig. S3.
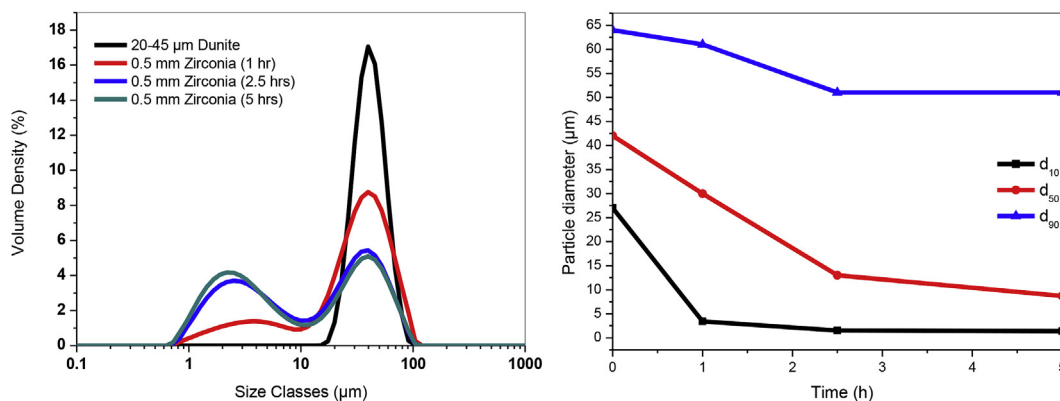
Fig. 4. SD for 20−45 μm dunite feed and following 1 hr, 2.5 h and 5 h concurrent grinding at 180 °C using 0.5 mm zirconia as grinding media with 50 wt% media and 15 wt%solids concentration (left). Variation of particle diameters with time (right).
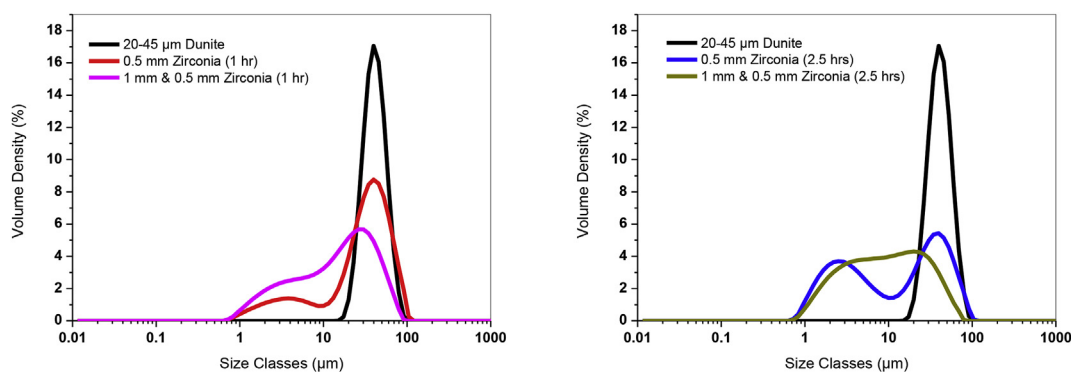
Fig. 5. PSD for dunite ground samples using 50 wt% media and 15 wt% solids at 180 °C, after 1 h grinding with 0.5 mm zirconia and 1 mm and 0.5 mm zirconia mixture (50:50 by mass) (left), after 2.5 h grinding with 0.5 mm zirconia and 1 mm and 0.5 mm zirconia mixture (50:50 by mass) (right).

Table 4
PSD for 20−45 μm dunite feed, 0.5 mm zirconia ground sample and 1 mm and 0.5 mm zirconia mixture (50:50 by mass) ground samples using 50 wt% media and 15 wt% solids at 180 °C.

| Grinding Media Size	Time (hr)	d_{10} μm	d_{50} μm	d_{90} μm
Feed	−	27	42	64
0.5 mm zirconia	1	3.4	30	61
1 mm and 0.5 mm zirconia mixture	1	2.2	15	43
0.5 mm zirconia	2.5	1.5	13	51
1 mm and 0.5 mm zirconia mixture	2.5	1.9	8.2	33

The data in Fig. 2 show that a mixture of 50 wt% media and 15 wt % solids provided optimum results for grinding (minimum d_{10}, d_{50} and d_{90}, Table 2) and generated a higher fraction of fine particles (Fig. S3 (b) Supplementary Information). These results disclose that the optimum overall slurry concentration is 54 wt% (Table 1), and the optimum mass ratio of grinding media to dunite solids is 3.3. These results, along with studies conducted in the clear acrylic reactor, assisted in establishing the conditions for concurrent grinding. Two principle requisites for conducting the concurrent grinding study were established. First, the ratio of the percentage of media and percentage of solids should be slightly higher than 3. Second, the media should partially sit at the base of the reactor with strong axial movement (Fig. S2 (g)) such that the falling grinding media would impact on the base media layer and enhance the grinding action. There are two mechanisms involved in grinding. First is grinding through the compression of the falling grinding media on the media present at the base. Second is through the shearing action between different media particles present at the base and is probably more dominant. The optimum solids concentration was found to be 15−25 wt%, as at higher concentrations of solids grinding media resulted in the development of a swirling motion (Fig. S2 (i)) and its effectiveness was reduced.

3.3. Effect of temperature on concurrent grinding

A mixture comprised of 50 wt% media (0.5 mm zirconia) and 15 wt% solids was selected for further study, to establish the effectiveness of concurrent grinding at 180 °C, which is the temperature often adopted for aqueous mineral carbonation of peridotites (dunite, olivine) rocks. A comparison of PSDs following 5 h of concurrent grinding at room temperature (25 °C) and at 180 °C shows significant enhancement in the effectiveness of grinding at the higher temperature. (Fig. 3, Table 3). This effect is attributed to the increased number of collisions at high temperature due to reduction in the viscosity and density of water. Knieke et al. (Catharina Knieke et al., 2011) observed no significant change in grinding behaviour as they varied temperature from 45 °C to −5 °C during grinding of tin oxide particles. In the present study, the feed material type and initial size is different to that of the tin oxide particles and the temperature employed during grinding is much higher (180 °C). Knieke et al. (Catharina Knieke et al., 2011) did not observe a significant change in viscosity, indicating that the 50 °C temperature change was not sufficient to cause an effect.
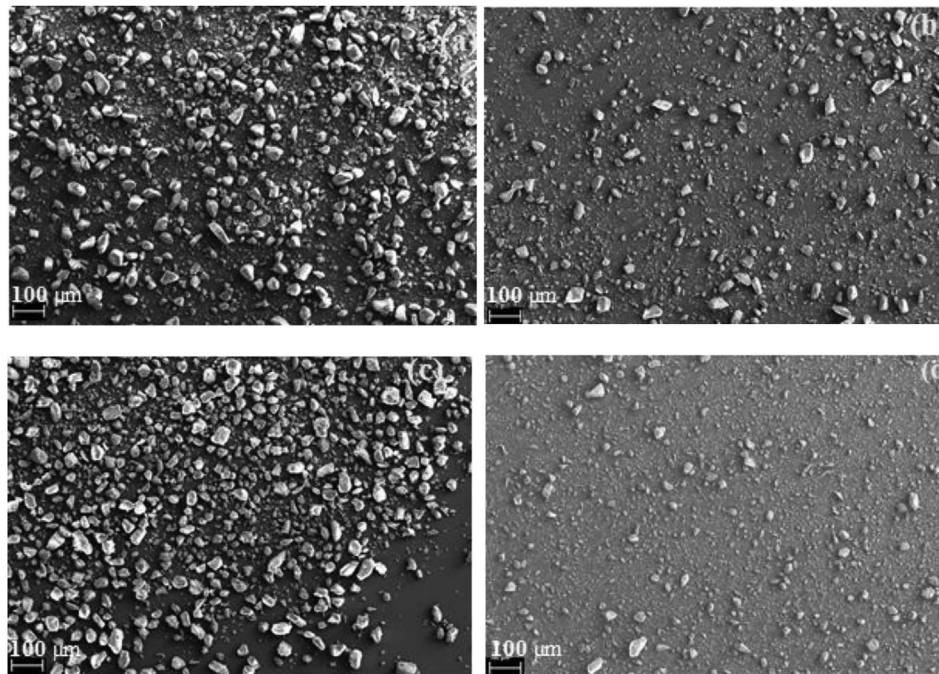
Fig. 6. SEM analysis of ground material (a) 0.5 mm zirconia after 1 h grinding (b) 1 mm and 0.5 mm zirconia mixture after 1 h grinding (c) 0.5 mm zirconia after 2.5 h grinding (d) 1 mm and 0.5 mm zirconia mixture after 2.5 h grinding.
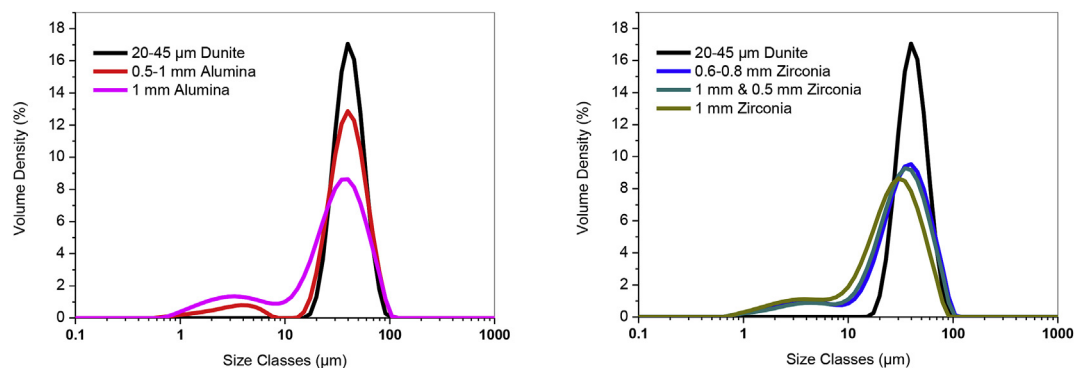
Fig. 7. PSD for dunite ground samples from reactor using 50 wt% media and 15 wt% solids at room temperature (1 h) using a range of media size, mixtures and types, alumina grinding media (left), zirconia grinding media (right).

Table 5
PSD for dunite ground samples using 50 wt% media and 15 wt% solids at room temperature (1 h) using different media size and composition.

|	d_{10} μm	d_{50} μm	d_{90} μm
Feed	27	42	64
0.5–1 mm alumina beads	18	36	59
0.6–0.8 mm zirconia beads	6.3	31	59
1 mm and 0.5 mm zirconia beads mixture (50:50)	7.2	29	57
1 mm alumina beads	3.4	28	57
1 mm zirconia beads	4.6	24	49

3.4. Selecting optimum time for grinding

To determine the optimum time for concurrent grinding, experiments were performed for 1 h, 2.5 h and 5 h, using 0.5 mm zirconia and 50 wt% media and 15 wt% solids concentration (Fig. 4). For grinding at 180 °C, no significant difference was observed

between 2.5 h and 5 h as compared with that achieved after 1 h suggesting 2.5 h as an optimum time for grinding. Fig. 4 show that there is no significant change in PSD between 2.5 h and 5 h. PSD decrease till 2.5 h and not afterwards so 2.5 h is optimum.

3.5. Selection of optimum media size and composition

High d_{90} values (Tables 2–3) indicate that larger particles are not significantly impacted or reduced in size (Fig. S3) by 0.5 mm zirconia. A mixture of 1 mm zirconia and 0.5 mm zirconia (50:50 by mass) grinding media was used for concurrent grinding experiments of 1 h and 2.5 h duration and results of these experiments are compared with the results where only 0.5 mm zirconia was used (Fig. 5). Experiments involving a mixture of media sizes shifted the bimodal distribution to unimodal (Fig. 5 (right)) and the resulting narrow PSD is indicative of equivalent extent of grinding of all particles sizes. Consequently this grinding media mixture was judged to perform better, compared to grinding using only 0.5 mm
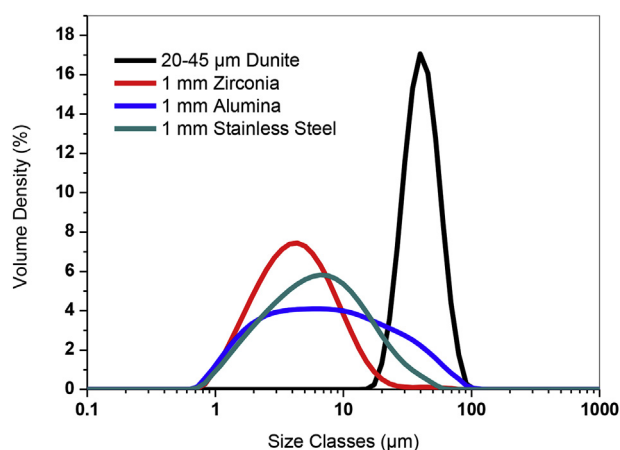
Fig. 8. PSD for ground samples from reactor. Comparison of experiments using 1 mm alumina, 1 mm zirconia and 1 mm stainless steel balls having same volume ($10\,cm^3$) at $180\,°C$ for 2.5 h grinding.

Table 6
PSD for ground samples from reactor for 1 mm zirconia, 1 mm alumina and 1 mm stainless steel balls having same volume ($10\,cm^3$).

	d_{10} μm	d_{50} μm	d_{90} μm
Feed	27	42	64
1 mm alumina	1.6	6.6	32
1 mm stainless steel	1.7	5.7	18
1 mm zirconia	1.6	3.6	9.6

zirconia, since it appears that larger diameter particles are ground ($d_{90} = 33\,\mu m$, Table 4). This difference is also evident from a cursory assessment of the corresponding SEM micrographs (Fig. 6(a−d)).

Different media size and compositions (0.5−1 mm alumina,

1 mm alumina, 1 mm zirconia, 0.6−0.8 mm zirconia and a mixture (50:50 by mass) of 1 mm and 0.5 mm zirconia) were studied for their efficacy in reducing PSD following 1 h of concurrent grinding (Fig. 7 and Table 5). 1 mm zirconia beads proved to be the most effective of the grinding media examined, followed by 1 mm alumina beads. 0.6−0.8 mm zirconia balls and a mixture of 1 mm and 0.5 mm zirconia beads (50:50) provided almost identical results. 0.5−1 mm alumina beads were the least effective of all the media studied. Samples which were ground using 1 mm zirconia beads showed more fine particles, followed by 1 mm alumina, mixture (50:50 by mass) of 1 mm and 0.5 mm zirconia beads, 0.6−0.8 mm zirconia beads and 0.5−1 mm alumina beads (Fig. S4 (a-f) Supplementary Information). The mode of action of the grinding media is apparent from the images presented in Fig. S4 (g-h), which shows deep pits in many of the particles and what appears to be fracturing of the particles at various angles.

A grinding media size of 1 mm appeared to be the optimum size for effective grinding, corresponding to a grinding media size to feed size mass ratio of 20. This finding is consistent with the study by Mankosa et al. (Mankosa et al., 1986, 1989) who also concluded that the optimum grinding media to feed size ratio to be 20.

3.6. Media efficacy during grinding experiments at constant volume

Alumina, zirconia and stainless steel media have a density of $3.9\,g/cm^3$, $6.0\,g/cm^3$ and $7.8\,g/cm^3$ respectively. Alumina, zirconia and stainless steel have a Vickers hardness of 1250−1700, 1043−1446, 697−865 HV respectively. To compare 1 mm zirconia, 1 mm alumina and 1 mm stainless steel balls as grinding media based on a constant volume of media (and an approximately constant number of grinding balls), experiments were performed using a $10\,cm^3$ volume of each medium. The 1 mm zirconia media had a significant effect on the final PSD of the reactor solids, where almost all of the feed material was converted into sub $10\,\mu m$ particles (Fig. 8& Table 6). SEM micrographs also confirm the transformation of the original material to fines is significantly increased for 1 mm
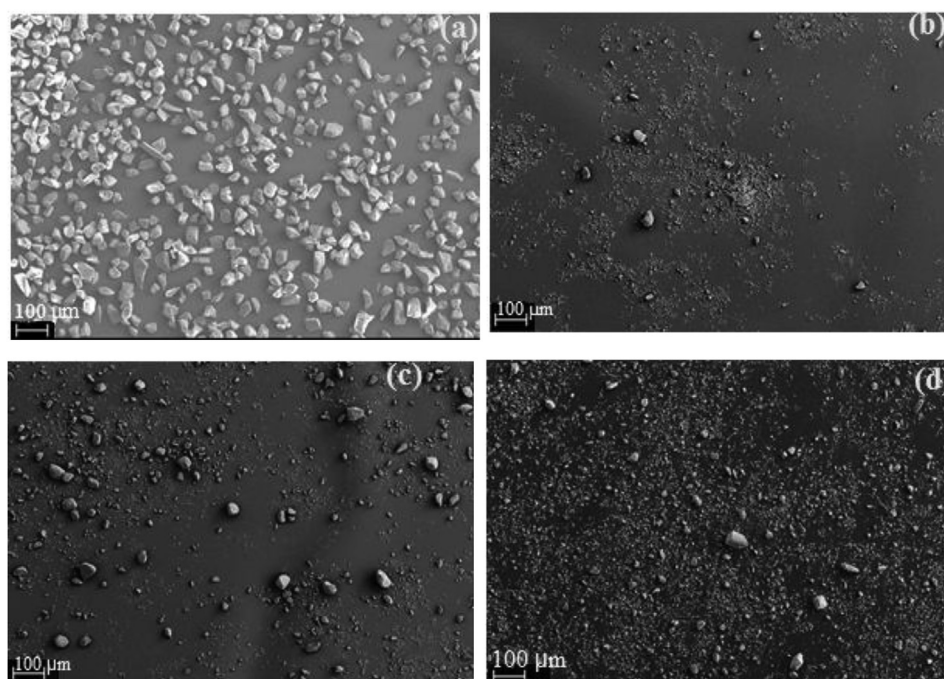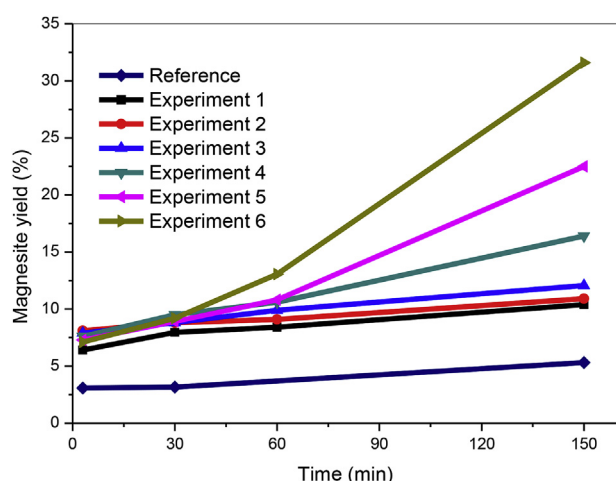

Fig. 9. 20-45 μm dunite feed and ground samples from reactor for experiments using 1 mm zirconia ($10\,cm^3$), 1 mm alumina ($10\,cm^3$) and 1 mm stainless steel ($10\,cm^3$) at $180\,°C$ for 2.5 h (a) 20−45 μm dunite feed (b) 1 mm zirconia ground (c) 1 mm alumina ground (d) 1 mm steel ground.

Table 7
Statistical experimental design and result (yield).

Experiment Identification	Slurry conc. (wt%)	Grinding media conc. (wt%)	Temperature (°C)	Pressure (bar)	Yield (%)
Reference	15	0	180	130	5.3
1	30	30	180	65	10
2	30	30	155	130	11
3	15	30	180	65	12
4	30	50	155	130	16
5	15	50	155	65	23
6	15	50	180	130	32

Table 8
Effect on yield with parameter at extreme.

Variable at Extreme	Yield
Grinding media conc. (50 wt%)	6.3
Slurry conc. (30 wt%)	−5
Pressure (130 bar)	2.3
Temperature (180 °C)	0.66

Table 9
PSD of feed, reference and concurrent ground samples. See Table 8 for a description of conditions in relation to experiments 1 to 6.

	d_{10} μm	d_{50} μm	d_{90} μm
Feed	27	42	66
Reference	25	40	66
Experiment 1	2.8	26	53
Experiment 2	1.7	30	57
Experiment 3	2.3	16	41
Experiment 4	1.9	9.4	30
Experiment 5	1.4	3.9	25
Experiment 6	1.5	3.9	22

Fig. 10. Magnesite yields comparison for reference experiment and concurrent grinding experiments. See Table 8 for a description of conditions in relation to experiments 1 to 6.

zirconia as compared to 1 mm alumina and 1 mm stainless steel (Fig. 9(a–c)). Density difference between zirconia and alumina is

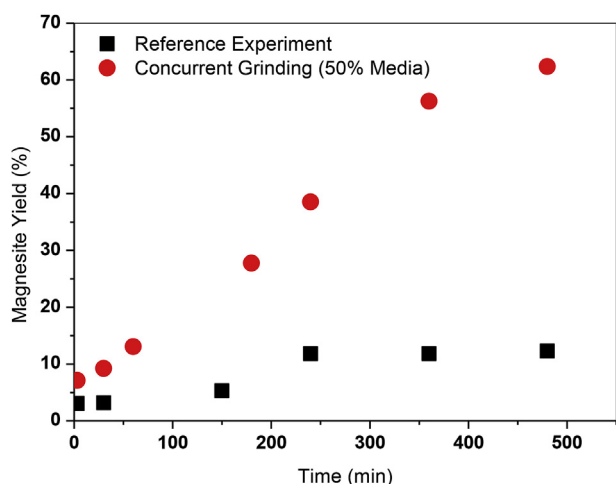**Fig. 11.** PSD of feed, reference and concurrent ground samples.

great as compared to difference between hardness. However, difference between zirconia and stainless steel hardness is great as compared to density. These density and hardness differences show that it is better to have media with high hardness and medium density. If media has high density (e.g. stainless steel) it does not lift properly during grinding. These media were compared based on equal volume, otherwise alumina media would have occupied more volume fraction due to low density.

3.7. Statistical experimental design for testing effect of slurry concentration, grinding media concentration, temperature, pressure and time on magnesite yield

To determine the effect of slurry concentration, grinding media concentration, temperature, pressure and time on magnesite yield during carbonation with concurrent grinding; statistical experimental design was performed adopting the Placket Burman technique (Placket and Burman, 1946) (Table 7) (refer to Supplementary Information for detail). This technique facilitates the identification of important variables and determines the quantitative effect that these variables have on magnesite yield. Nominal (low) and extreme (high) values of variables such as slurry and grinding media concentration were selected as key variables based on clear acrylic reactor studies and PSD results, while a reaction temperature of 155 °C is the optimum for lizardite carbonation and 180 °C is optimum for olivine carbonation (Gerdemann et al., 2007; Connor et al., 2005). Reference experiments, in which grinding media was not employed were also performed for benchmark comparison and 20–45 μm dunite was used as feedstock for all experiments conducted for this part of our research.

The increase in grinding media concentration from 30 wt% to 50 wt% had the largest effect on magnesite yield (Table 8). A high slurry concentration (30 wt%) had a negative effect on magnesite yield when compared to low slurry (15 wt%) concentrations. High pressures (130 bar) had a positive effect on magnesite yield compared to low (65 bar) pressure experiments. High temperature (180 °C) had a (slightly) positive effect on magnesite yield compared to yields at experiments performed at 155 °C. This aspect

Fig. 12. Magnesite yield for reference and concurrent grinding experiment. Reference experiment is performed without grinding media and concurrent ground experiment is performed using 50 wt% media (1 mm zirconia), 15 wt% solids slurry using 0.64 M NaHCO$_3$ at 180 °C temperature and 130 bar pressure.

of the study also showed (quantitatively) that grinding media concentration is the most important variable, followed by slurry concentration, pressure and temperature on influencing magnesite yield. Concurrent grinding led to an increase in final magnesite yield approximately six times greater than that the yield obtained from the reference benchmark experiments (Fig. 10).

We acknowledge that number of experiments should have been more for statistical experimental design. Here our results are based on testing each variable three times at its low level and three times at its high level (refer to Supplementary Information for detail). 50 wt% media and 15 wt% slurry concentration provided best yields (32% and 23%) under carbonation (Table 7) and this combination (50 wt% media and 15 wt% slurry) also provided best particle size reduction under simple grinding tests (Table 2). When both of these results match, we did not consider further examination through statistical experimental design.

PSD measurements (Fig. 11, Table 9) wereperformed on carbonated products, and the analysis showed that a higher fraction of fine carbonated samples is associated with higher magnesite yields.
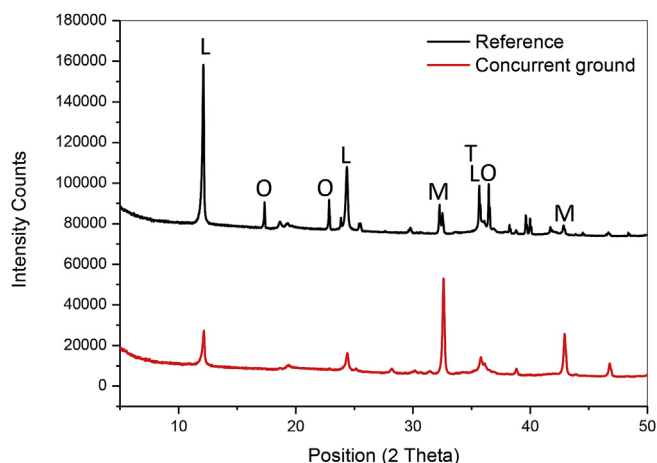
Fig. 13. XRD analyses of concurrent grinding experiment and reference experiment,O=Olivine, L = Lizardite, M = Magnesite, T = Magnetite.

3.8. Raw dunite carbonation with concurrent grinding

In response to these results, extended 8 h experiments using raw 20–45 μm dunite (without heat-activation) wereperformed using the optimised reaction conditions of concurrent grinding established from the statistical design experiments i.e 50 wt% media, 15 wt% slurry at 130 bar using 0.64 M NaHCO$_3$. This resulted in a yield of 62.3% after 8 h (Fig. 12). Reference experiments were performed under similar reaction conditions in the absence of grinding media.

XRD analyses (Fig. 13) show that olivine was almost completely consumed during reaction, with only trace quantities remaining, while lizardite was partially consumed. A higher magnesite XRD reflection intensity was observed in the concurrent ground sample as compared to the reference experiment.

3.9. Concurrent (in operando) compared to in situ grinding

A 20–45 μm dunite sample was ground at 180 °C for 8 h using 1 mm zirconia (50 wt%). This prepared feed was carbonated in a second step for 8 h at 130 bar, 180 °C, 15 wt% solids and using 0.64 M NaHCO$_3$. This provided magnesite yields for *in situ* grinding experiments in which grinding and carbonation occur in separate steps. The yield obtained with *in situ* grinding was compared with the results of the concurrent (*in operando*) grinding experiments.

Concurrent (*in operando*) grinding during carbonation under the same conditions of pressure, temperature and solids loading resulted in higher final magnesite yields compared to *in situ* grinding experiments (Fig. 14). This finding is consistent with that reported byJulcour et al. (Julcour et al., 2015). They prepared *in situ* grinding (two-step mode) feed at room temperature. In the current study, the carbonation feed used was prepared at 180 °C to engender the same PSD (Fig. 14) for both experiments and gain insight into the mechanism of the two (*in situ* and *in operando*) experimental protocols.

In situ grinding produces relatively high magnesite yields at the start of the experiment (initial 4 h), presumably due to the presence of an elevated concentration of fines in the feed and subsequently (from 4 h to 8 h) concurrent (*in operando*) grinding yields are higher by comparison. Julcour et al. observed a similar trend during their *in situ* (two-step) mineral carbonation studies (Julcour et al., 2015). Overall, high yields for both concurrent and *in situ* grinding show that mechanism behind grinding is to reduce particle size and it is of little importance whether it occurs concurrently or *in situ*. Significant reduction in particle size in both concurrent and *in situ* grinding was observed as feed particles were converted into sub 10 μm particles (Fig. 14-right).

### 3.10. Effect of sampling on magnesite yield

Four individual experiments were performed to study the effect of sampling (of reactor contents) on magnesite yield. Experiments without sampling were performed for 2.5 h, 60 min, 30 min and 3 min respectively. Comparable yield results (Fig. 15) with and without sampling was demonstrated confirming the minimal influence of sampling on progressive yield calculations.

5. Conclusions

For our system, 50 wt% media and 15 wt% slurry concentrations were favoured in terms of particle size reduction, in which the ratio of percentage of grinding media to percentage of solids was 3.3. Grinding media concentration should be selected such that the media sits partially as a layer at the base of the reactor so that falling media balls impact on this media layer to engender grinding action.
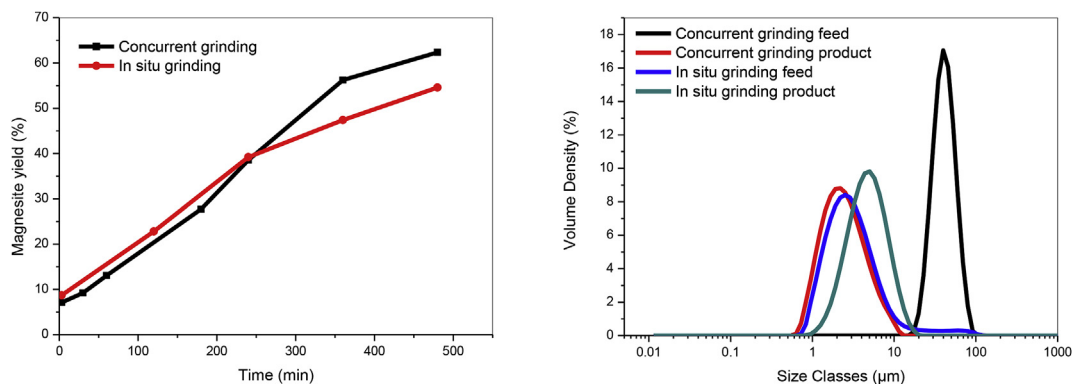
Fig. 14. Magnesite yield for concurrent (*in operando*) grinding and *in situ* grinding (left), concurrent ground experiment is performed using 50 wt% media (1 mm zirconia), 15 wt% solids slurry using 0.64 M $NaHCO_3$ at 180 °C temperature and 130 bar pressure. *In situ* grinding experiment feed is prepared using 50 wt% media (1 mm zirconia), 15 wt% solids slurry at 180 °C for 8 h. In second step this feed is carbonated using 15 wt% solids slurry using 0.64 M $NaHCO_3$ at 180 °C temperature and 130 bar pressure, PSD for concurrent grinding feed, concurrent grinding product, *in situ* grinding feed and *in situ* grinding product (right).
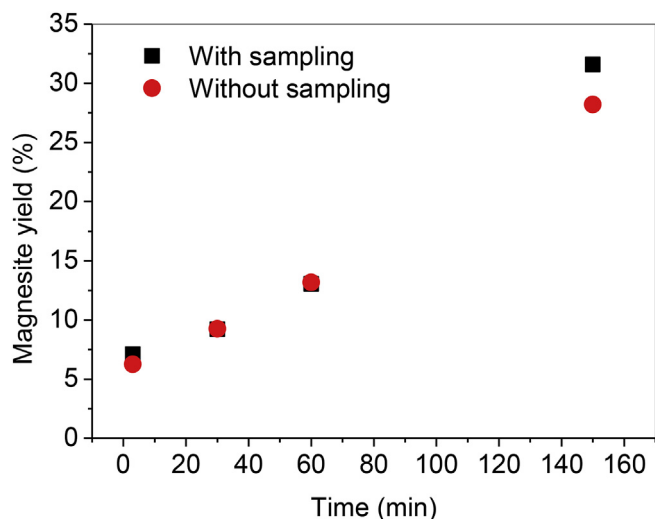
Fig. 15. Magnesite yield with sampling and without sampling using 1 mm zirconia media.

Maximum solids concentration was found to be 15 wt%. With a higher solids concentration the grinding media commenced as wirling motion with the solids, with an associated reduction in effectiveness.

Grinding performance was enhanced at elevated temperatures (180 °C). Concurrent (*in operando*) grinding was tested for 1 h, 2.5 and 5 h and 2.5 h time proved to be the optimum time. A mixture of 1 mm zirconia and 0.5 mm zirconia (50:50 by mass) was the preferred grinding media compared to 0.5 mm zirconia. When different media size and compositions were examined, 1 mm zirconia beads proved to be the most efficient grinding media, followed by 1 mm alumina beads. The optimum grinding media size to feed particle size ratio was 20.

Grinding media tests at constant volume disclosed that 1 mm zirconia media resulted in a significant reduction in PSD compared to 1 mm stainless steel and 1 mm alumina beads. 1 mm zirconia media converted virtually all the feed into sub 10 μm size fraction during 2.5 h grinding at 180 °C. These results show that it is better to have media with high hardness and medium density.

In carbonation experiments with concurrent grinding, grinding media concentration had the most significant effect on magnesite yield. A high slurry solids concentration (30 wt%) had a negative effect on magnesite yield as compared to low slurry solids concentration (15 wt%). High pressure (130 bar) had a positive effect on magnesite yield when compared to low pressure (65 bar), and high temperature (180 °C) had a (slightly) positive influence on the magnesite yield as compared to yields obtained at a reaction temperature of 155 °C. The parameters in order of importance influencing magnesite yield were found to be grinding media concentration followed by slurry solids concentration, pressure and temperature. Using optimised conditions as determined from statistical experimental design, a magnesite yield of 62% was attained in carbonation of raw 20—45 μm dunite without heat-activation. XRD analysis showed that brucite and olivine were almost completely consumed while lizardite was partially consumed. Concurrent (*in operando*) grinding also provided higher yields as compared to *in situ* grinding.

We conclude that concurrent grinding may be a suitable technique for the processing of feedstocks such as those containing significant proportions of forsterite and pyroxene, minerals which are unresponsive to thermal activation for use in aqueous mineral carbonation.

Acknowledgment

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jclepro.2018.11.189.

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